Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

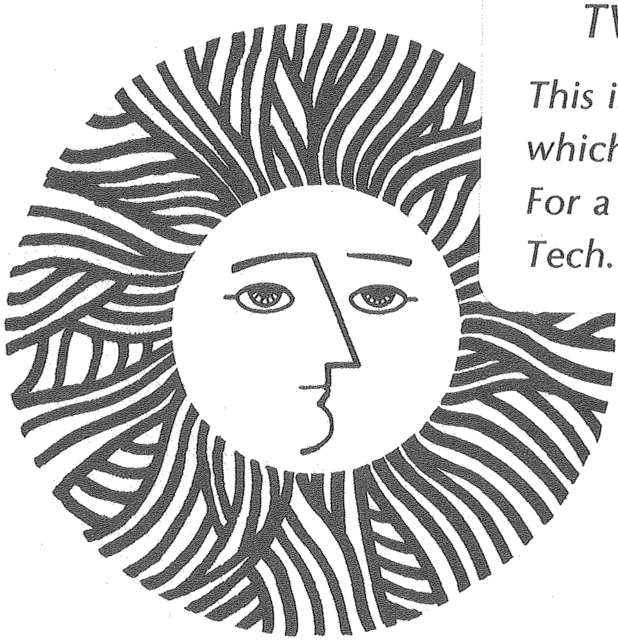
ENERGY & ENVIRONMENT DIVISION

Presented at the Tenth Thermochemical Conversion Contractors' Meeting, Berkeley, CA, February 12-13, 1980

CATALYTIC BIOMASS LIQUEFACTION

Sabri Ergun, Carlos Figueroa, Cihan Karatas, Larry Schaleger, Manu Seth, James Wrathall and Nasser Yaghoubzadeh

February 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

CATALYTIC BIOMASS LIQUEFACTION

Presented at the
Tenth Thermochemical Conversion Contractors' Meeting
Biomass Energy Systems Branch
Berkeley, California

February 12-13, 1980

by Sabri Ergun, Carlos Figueroa, Cihan Karatas,
Larry Schaleger, Manu Seth, James Wrathall and
Nasser Yaghoubzadeh

Lawrence Berkeley Laboratory
Berkeley, California 94720

INTRODUCTION

The Department of Energy's Biomass Liquefaction Test Facility (BLTF) at Albany, Oregon, was built in 1976. Its design was based on a process conceptualized by the Bureau of Mines in the early 1970s. This process utilizes anthracene oil as the start-up vehicle for liquefying wood flour. The first operator of the plant, Bechtel Corp., was unable to produce significant quantities of oil owing to a combination of plugging problems and equipment failures. A major process unit, the stirred tank reactor, could not be operated due to a design deficiency, and another, the centrifuge, had to be bypassed due to operational difficulties. Therefore, Bechtel was unable to demonstrate process feasibility.

In October, 1977, LBL assumed responsibility for monitoring the Albany development program. LBL was given the task of evaluating progress, providing technical support and making periodic recommendations to DOE regarding operations. When Rust Engineering took over operation of the facility in 1978, LBL was also given the responsibility of issuing operating directives for test runs to be conducted at Albany. LBL also initiated a program of in-house engineering support and bench-scale research to explore optional approaches to biomass liquefaction. This research led to the development of the so-called LBL process option in which wood ships are prehydrolyzed and introduced into the liquefaction reactor as an aqueous slurry rather than a carrier oil slurry as in the BOM scheme. Advantages of the LBL process appeared to be two-fold. First, costly drying and grinding of wood chips was avoided. Second, it seemed likely that biomass could be pumped into a high pressure reactor at higher concentration than had been possible with the BOM process.

In 1979, in response to an LBL operating directive, Rust Engineering succeeded in producing six barrels of purely wood-derived oil by the LBL process option. Unfortunately, due to equipment limitations, the acquisition of firm engineering data from that run, including material and energy balances, was not possible. One important question remaining unanswered was whether aqueous biomass slurries could be pumped at concentrations higher than 10%. Economic feasibility requires that biomass be pumped at concentrations in excess of 20%. Nevertheless the run established the chemical feasibility of the LBL process on a pilot scale. This is yet to have been demonstrated in the case of the BOM process, although Rust Engineering is preparing to conduct a modified BOM process test run in the near future.

LBL reported progress on two major fronts at the 9th Quarterly Thermochemical Contractors' Meeting at Rolla, Missouri, in November, 1979. An important new development in the preparation of pumpable, concentrated biomass slurries was announced, and progress in the fabrication of a bench-scale continuous tubular reactor for liquefaction was detailed. This report, which covers the first quarter of FY80 (October through December, 1979) concerns three tasks: 1. Preparation of biomass slurries; 2. Characterization and flow properties of concentrated slurries; 3. Construction of biomass liquefaction process engineering unit (PEU).

HIGHLIGHTS OF THE QUARTER

- Homogenized aqueous wood slurries are produced from wood chips at concentrations greater than 30% by hydrolysis-refining.
- Technical feasibility of continuously pumping concentrated, homogenized wood slurries is demonstrated on pilot scale at Albany BLTF.
- Construction of LBL Process Engineering Unit (PEU) - a continuous tubular reactor - is completed and shakedown tests have begun.

PREPARATION OF BIOMASS SLURRIES

The problem of continuous injection of woody biomass into a high pressure reactor has been approached in three different ways. In the original BOM process, wood chips were dried, ground to -60 mesh flour and slurried with anthracene oil. In the University of Arizona concept, wood is plasticized and extruded at high pressure directly into the reactor. The approach developed at LBL involves comminution of wood chips by means of acid-catalyzed hydrolysis and subsequent injection into the liquefaction system as an aqueous slurry. Progress made on the LBL approach is summarized.

The objective was to determine the highest concentration at which a prehydrolyzed wood chip slurry would retain its pumpability. Wood chips (25 to 33% by weight, oven-dry basis) and water were reacted in a 1-gal autoclave at pH 1.44 and 200°C for 30-min. The pumpability of the product was evaluated by inspection. It appeared that the product derived from wood at an initial concentration of 30% retained the characteristics of a liquid whereas that from wood at 33.3% was a solid. Thus an upper concentration limit of 30-33% is indicated. However, this limit is subject to upward revision depending upon the degree of subsequent physical modification, e.g., refining (see below). Results and reaction conditions are shown in Table 1.

TABLE I

Hydrolysis of Concentrated Slurries of Wood Chips[a]

Run	Liquor/Wood Ratio	Conc.	Mass Recovery	Biomass Product Soluble	Biomass Product Insoluble
33	3.0	25 %	90%	6%	12%
27	2.5	28.6%	96%	5%	14%
32	2.3	30 %	92%	3%	24%
31	2.0	33.3%	90%	3%	26%

[a]Conditions: pH 1.44 (sulfuric acid); temperature, 200°C; residence time, 30 min.

REFINING-HOMOGENIZATION

We reported at the Rolla meeting that several days' stirring of a concentrated prehydrolyzed wood slurry produces a suspension that appears stable with respect to the settling out of solid particles. It was then learned that a similarly stable suspension could be formed with several minutes of agitation in a Waring blender. A small-scale test pumping system was designed and installed; preliminary tests indicated that the new material was pumpable. These observations suggested that homogenization was the ultimate key to the production of truly pumpable slurries and led to the notion that such homogenization might be achieved through the application of disc refining, a commercial process used extensively in the pulp and paper industry to separate wood pulp into fibers.

Thus, arrangements were made to use a 14-inch Bauer refiner available through the courtesy of the Wood Products Laboratory of Oregon State University at Corvallis. A cooperative project between LBL and Rust Engineering was initiated to (1) make several barrels of prehydrolyzed wood slurry at the Albany facility; (2) refine the slurry at OSU; and (3) conduct pumping tests under various conditions of flow, concentration and temperature at Albany. An engineering data base for the design and installation of a slurry handling system has thus been established. Biomass has now been pumped continuously at concentrations greater than 24%.

CHARACTERIZATION AND FLOW PROPERTIES OF CONCENTRATED SLURRIES

The results of the Albany pumping tests were extremely encouraging. They showed that freshly prepared slurry was more amenable to pumping than the aged slurry that had been used in preliminary experiments* using glass coils conducted at LBL. The success of these tests allowed us to design a slurry handling system that should eliminate problems with the front end of the process that have dogged operations at Albany since its inception.

The action of the disc refiner on hydrolyzed wood slurry produces a molasses-like fluid which does not settle or clog in its fresh condition. Several other important observations have been made that may contribute to the formulation of a theoretical treatment of flow properties. For example, most slurries show viscosities not markedly different from that of the pure liquid phase or suspensor. The homogenized wood slurry is unusual in that, at a given temperature and flow rate, suspensor viscosity is magnified 100-1000 times by particle interaction.

Inspection of slurry flowing in a glass coil shows interlocking particles moving as a plug surrounded by a lubricating film of water. This apparent lack of laminar profile has important ramifications in both heat and mass transfer.

---

* See J. Wrathall and S. Ergun, "Hydrolyzed Wood Slurry Flow Modeling," LBL Report No. 10090, November, 1979.

The tests at Albany also underlined the shear-thinning nature of the slurry, where a doubling of the flow rate resulted only in a 15% increase in the pressure drop. While not of particular process importance, this fact suggests a model in which strong interparticle interaction results in hindered flow.

In early pumping tests at LBL, we were unable to pump slurries less than 8.5% in total solids because of plugging. Settling out probably occurs when particles start to behave independently and gravity outweighs the forces of interparticle attraction. This would occur either when there are not enough particles to interlock in plug flow or when the particles are widely distributed in size. Process economics preclude the former possibility while proper homogenization eliminates the latter.

The following major conclusions have been drawn from the above studies on flow properties of prehydrolyzed-refined wood slurry:

1. Apparent viscosity is a function of suspensor viscosity and interparticle interference.

2. Slurry particles interlock during laminar flow, resulting in pseudo-plug flow.

3. Apparent viscosity decreases with linear velocity, while solids holdup increases.

4. Gas uptake increases apparent viscosity.

5. Settling occurs <u>BELOW</u> a critical total solids concentration.

CONSTRUCTION OF BIOMASS LIQUEFACTION PEU

The decision to construct such a unit was made in late 1978 for two reasons. First, the stirred tank reactor configuration installed at Albany is not scaleable to commercial size. Second, the technical feasibility of an oil-recycle (BOM) process had never been established. Thus, LBL decided that additional basic research was required to define a workable liquefaction scheme as well as to provide direct scaling data for eventual commercialization.

Design and procurement activities were begun January, 1979. A heavy equipment room became available in June, 1979, and required plumbing and electrical modifications were begun in September. Assembly of the PEU was underway by that time and largely completed by the end of December. Also, the reactor's air heater recirculation system, the gas feed compressor and the pressure let-down system were each tested individually. A schematic of the integrated unit is shown in Fig. 1.

Cold tests of the high pressure water/gas system are currently underway; these are to be followed by high temperature and pressure system tests, slurry recirculation system tests, and, by mid-April. initial liquefaction runs.

CONTRACT EXPENDITURES

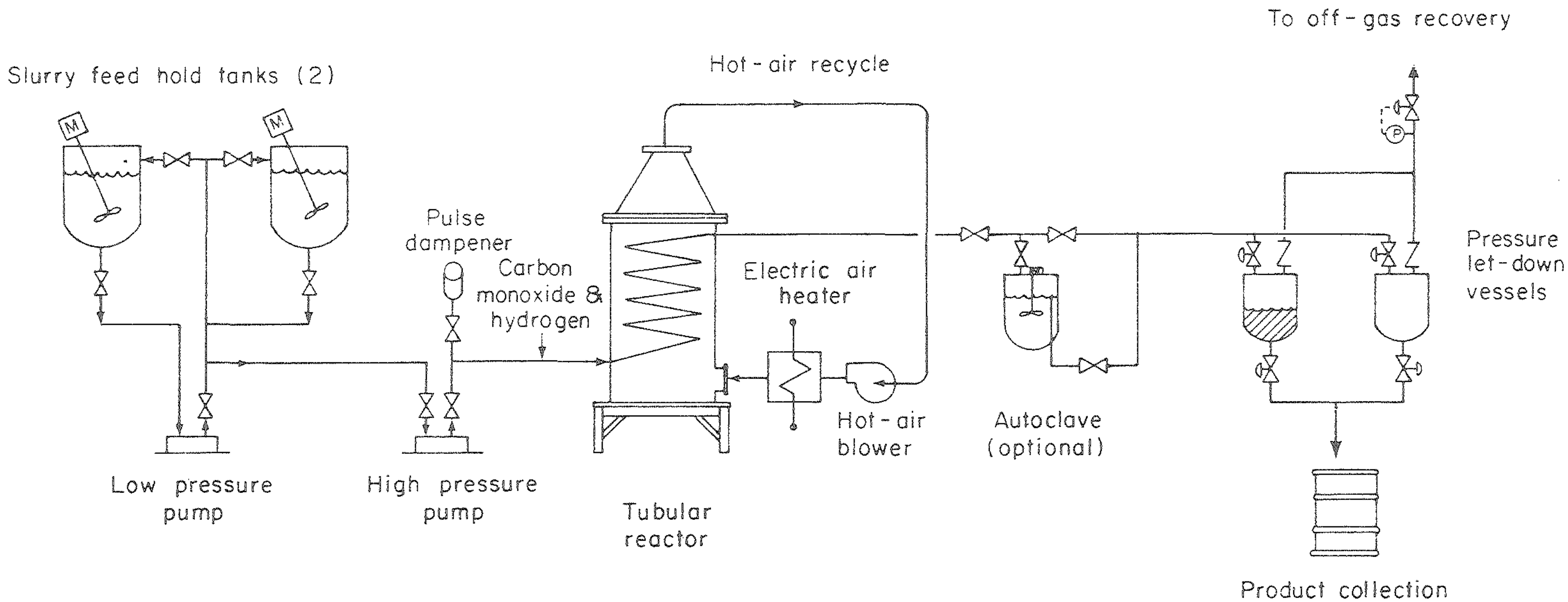
Expenditures to date are on target. Although monies have not actually been distributed as of this writing, the expected FY80 level of funding is $680,000. As of the end of December, 1979, approximately $170,000 (25%) had been spent or encumbered.

THIS QUARTER'S ACTIVITIES

During the second quarter of FY80, the following activities will be undertaken.

- Commission and Test PEU
- Design and Install Control System Based on Product Slurry Flow Properties
- Develop Flow-Measuring Device for Use at Low Linear Velocities
- Process Evaluation and Optimization
  - Gas and Slurry Recycling
  - Reactor Design
  - Heat Transfer Media
- Investigate Chemical Fate of Water-Solubles under Liquefaction Conditions
- Initiate Screening of Nonaqueous Solvent Systems

- Investigate Degassing of Prehydrolyzed-Refined Slurry
- Conduct Batch Studies on Carbonate - Catalyzed Liquefaction to Provide Operating Conditions for Start-up of PEU.



Biomass liquefaction process evaluation unit

LBL process

XBL 7910-4293

FIGURE 2